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(54) DENDRITE POWDER MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a highly conductive paste material inexpensively in a safe manner for the environment, by making a surface contact with a predetermined plating solution for the growth of dendrites, coating them, powdering them and adding a polymeric material to them.

SOLUTION: A surface resistant to plating is made in contact with an electrolyte or electrodes plating solution to grow dendrites, which are then coated. These coated dendrites are separated from the plating-resistant surface, are powdered and are mixed with environment-friendly flux for the formation of a conductive paste material dispersed in a thermoplastic or thermosetting polymer matrix. In those processes, the dendrite-growing material is selected from the group comprising Cu, Pd, Pt, Ni, Ag and Au, the coating material from the group comprising In, Sn, Zn, Pb, Bi and Sb, and the polymeric material from the group comprising polymeric resins such as polyinide and siloxane.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to dendritic powder useful to the paste for forming conductive connection between conductive members, and the application to the electronics.

[0002]

[Description of the Prior Art] Almost all the electric conductors used for an electronic instrument are built with copper, aluminum, gold, silver, lead/tin (solder), molybdenum, and other metals. The soldered-joint technique which uses lead / tin alloy has played the important role on various level of electronic packaging, such as flip chip bonding (C4), solder ball connection in a ball grid array (BGA), and installation of the IC package to a printed circuit board (PCB). The solder joint formed in electronic packaging is important for electric interconnect, and a machine/physical connection. Even if any of these functions are not attained, a solder joint is considered to be failure and has a possibility that the whole electronic system may stop.

[0003] When including micro electronic packaging in a printed circuit board, the Pb-Sn eutectic solder (Sn63%, Pb37%) of the minimum [melting point] (183 degrees C) is most widely used in lead and the alloy of tin. By such Field of application, two kinds of soldered-joint techniques, a plating through hole (PTH) and surface mount technology (SMT) soldering, are used for mass production method. The fundamental difference among these two kinds of techniques is produced from the design of a printed circuit board, and the difference in the interconnect approach.

[0004] Micro electronic packaging is attached in the front face of an immediate printing circuit plate in SMT soldering. The main advantages of SMT are that the consistency of packaging becomes high, and this is realized by attaching components in both sides of a printed circuit board while eliminating almost all PTH in a printed circuit board. Furthermore, an SMT package has a fine lead pitch compared with the conventional PTH package, and a package miniaturizes it. Therefore, SMT is contributing to the miniaturization of electronic packaging, and the pan remarkably at the system-wide miniaturization.

[0005] In SMT soldering, soldering paste is applied to a printed circuit board by screen-stencil. Soldering paste consists of the fines, the flux, and the organic vehicle of solder. Into a reflow process, the particle of solder fuses, flux is activated, a solvent evaporates, the solder fused at coincidence unites, and, finally it solidifies. On the contrary, at a wave-soldering process, flux is first applied to a printed circuit board, and components

are arranged on it. Then, it solders by moving and soaking, after that melting solder waves.

[0006] A soldering process will be completed if a residual flux ingredient is removed usually applying a connection to a cleaning process. The harmful cleaning agent of CFC (chlorofluocarbon) currently used for this purpose and others is eliminated for an environmental problem, and in order to make a cleaning process into the minimum or to skip it, water solubility or a no clean flux ingredient is used.

[0007] By the latest development of a micro electronic instrument, very fine connection (the base of hundreds of microns) of a pitch is called for between electronic packaging and a printed circuit board. The current soldering paste technique used for SMT is not fit for interconnect of such a very fine pitch for the defect of soldering, such as bridging and solder boring. The limit on one technique in which I accept it on use of Pb-Sn eutectic solder is the high reflow temperature of about 215 degrees C. This temperature is higher than the glass transition temperature of the epoxy resin already used for the ingredient of almost all printed circuit boards. By exposing to this reflow temperature, a remarkable heat strain arises in the perpendicular direction especially on the surface of a printed circuit board in the printed circuit board after soldering. This is because structural reinforcement is not made in the direction. For this reason, the dependability of electronic system is remarkably spoiled by the residual heat strain of the assembled printed circuit board.

[0008] The serious problem for the pan about use of the solder containing lead (Pb) is an environmental problem which are other industries, already experiences and came to eliminate lead from a gasoline or a coating.

[0009] The conductive paste (ECP) is considered by electronic industry with the solder which does not contain two kinds which may become the substitute of the solder ingredient containing Pb of different groups' ingredient, i.e., lead. This invention describes development and application of a conductive paste ingredient. A conductive paste (or adhesives) blends the particle of filler metal into the matrix of a polymer ingredient, and is built. Although what kind of polymer is sufficient as it as long as a polymer matrix is used in the form of a paste also by thermoplasticity or thermosetting, epoxy, polyester, a polyimide siloxane, and its polyimide are desirable. The fusibility ketal and acetal diepoxide which were indicated by fusibility epoxy, especially the United States patent application/[08th] No. 210879 specification are desirable. This indication is included in this specification by reference. If drawing 1 is referred to, the epoxy 4 filled up with the silver granule child 2 is the most general example of the conductive paste 6, and what was placed between the front face 8 and the front face 10 is shown as schematic drawing. A silver granule child usually gives conductivity according to a percolation device by the shape of a flake, and an epoxy matrix performs adhesion with components and a substrate. The epoxy ingredient filled up with this silver is used in the electronic applicable field as a die-bonding ingredient for many years, and good thermal conductivity is used rather than that conductivity. However, this ingredient is not received in high conductivity and an application to be connected [of a pitch] fine. the silver migration with low connection resilience to which contact resistance will increase if it exposes to heat with low conductivity, and a rework are difficult for the epoxy ingredient filled up with silver -- etc. -- there are some limits. In order to show conductivity in all the directions, the epoxy ingredient filled up with this silver is

classified as conductivity is "isotropy." This has the electroconductive glue (or coat) of a different class, and this shows conductivity only in the one direction. This kind of ingredient is called "anisotropy" electroconductive glue coat 12, and schematic drawing is shown although the conductive particle 14 is contained in a binder or adhesives 16 in drawing 2 . Anisotropy electroconductive glue or a coat 12 shows conductivity, only when it compresses between two conductive front faces 18 and 20 to be shown in drawing 3 . Heat and a pressure are usually needed for this process. The applications with a main anisotropy electric conduction coat are adhesion to the printed circuit board of a liquid crystal display panel. The conductive particle 14 is usually deformable, for example, the plastic bowl coated with a solder ball or nickel, and gold is used for it. Most of a binder or adhesives 16 is thermosetting resin.

[0010] ECP manufactured by the powder and polyimide siloxane resin of the copper which carried out tin plating is a good candidate who replaces elevated-temperature solder joints, such as conte RORUDO collapse chip connection (C4) and solder ball connection (SBC) with a ceramic substrate. However, in the case of the printed circuit board of a polymer, this ECP is unsuitable. This is because the reflow temperature of 250 degrees C is far higher than the glass transition temperature of polymer resin, such as FR-4. The candidate for this purpose is ECP which blended with polyimide siloxane resin the powder of the copper which plated the indium. The reflow temperature of the paste of the powder of the copper which plated the indium is considered to be about 180 degrees C, and this is still lower than 215 degrees C which is the reflow temperature of Pb-Sn eutectic solder.

[0011] The compound paste ingredient of solder and a polymer is indicated by the U.S. Pat. No. 5062896 specification. This ingredient blends the filler of fusible solder powder, such as a lot of Bi-Sn, Pb-Sn, and Bi-Sn-Pb alloys, with thermoplastics, such as a small amount of polyimide siloxane, and a little flux agent. The connection of the solder united in part which does not contain an oxide is obtained, and this connection is strengthened with a polymer, it is low reflow temperature or can be reworked under existence of the solvent of a polymer.

[0012] Fusible electroconductive glue is indicated by the U.S. Pat. No. 5286417 specification. These adhesives serve as alloy fillers, such as Sn-Au and Bi-Au, from the thermoplastics with which glass transition temperature agrees with the melting point of the alloy of filler metal. The amount of the conductive ingredient in a polymer is about 15 - 20 % of the weight.

[0013] A flux agent and the adhesives containing metal particles, such as Sn, Pb, In, Bi, Sb, Ag, etc. which are used for reflow soldering, are indicated in the matrix of an epoxy resin by the U.S. Pat. No. 5136365 specification. By reflow soldering, the above-mentioned adhesives form the electrical installation of an anisotropy between an electrical part and a substrate.

[0014] The directive conductive polymer containing the powder of the filler metal of nickel or Cu is indicated by the U.S. Pat. No. 5213715 specification. This filler metal is processed with a different polymer from the polymer used as matrix resin. By compression, the polymer by which coating was carried out dissolves and conductivity is formed between filler particles.

[0015]

[Problem(s) to be Solved by the Invention] The purpose of this invention is safe for an

environment, and is to offer the process of a cheap conductive paste ingredient.
[0016] Other purposes of this invention are to offer the process of a conductive paste ingredient with conductivity higher than the epoxy resin filled up with conventional silver.
[0017] Other purposes of this invention are to offer the process of the conductive paste ingredient which can be processed at temperature lower than the reflow temperature of Pb-Sn eutectic soldering paste.
[0018]
[Means for Solving the Problem] The large mode of this invention is the approach of having the process which the front face which can be plated is contacted in the 1st plating liquid, and dendrite crystal is grown up from the 1st plating liquid on the above-mentioned front face, coats dendrite crystal, and forms the dendrite crystal by which coating was carried out.
[0019] The pan of the approach of this invention is coated with dendrite crystal in a specific mode with a conductive ingredient.
[0020] The powder of the dendrite crystal by which was separated from the front face which can plate the dendrite crystal by which coating was carried out by the pan of the approach of this invention in the specific mode, and coating was carried out to it is formed.
[0021]
[Embodiment of the Invention] According to the example of this invention, the powder of the copper coated with the thin film of low-melt point point metals which do not contain Pb, such as Sn, In, Bi, Sb(s), and these alloys, is mixed with a flux agent safe for an environment, and the conductive paste (ECP) ingredient distributed in the matrix of a thermoplastic or thermosetting polymer is indicated. The fine structure of ECP containing Cu powder which coated Sn is shown in drawing 4 .
[0022] In the specific example, the copper powder coated with the indium, polyimide siloxane resin, a solvent (NMP), no clean flux, and the new conductive paste ingredient that consists of a carboxylic acid/a surfactant are indicated. After carrying out sequential electrodeposition of the copper dendritic powder on a dummy substrate, the copper powder coated with the indium makes the dendritic powder of this copper electrodeposit an indium further, and is manufactured. Instead of copper dendritic powder, nickel, cobalt, chromium, palladium, platinum, etc. may use other dendritic powder. Instead of an indium, Sn, Zn, Pb, Bi, Sb(s), or these alloys can be used. Since the aspect ratio is large, dendritic powder has the advantage of having the electrical conductivity superior to globular form powder, thermal conductivity, or its both. Junction processing can be performed near 157 degree C which is the melting point of In. At this temperature, metallic bond between In, In, In and Au, or In and Cu (metallurgical bonding) is performed between the particle of dendrite crystal, and a particle, and between the particle of dendrite crystal, and a substrate. Also to a metal with soldering difficult for an indium metal and an alloy, such as aluminum, titanium, molybdenum, and a tungsten, since [being good] it gets wet and a property is shown, the ingredient of this invention is applicable also to junction of a liquid crystal display. Junction processing may be based on a solid-liquid reaction also by the solid state. According to the formula of a paste, the hardening process of a polymer is also combinable with a junction process. Conductivity higher than metallic bond and the case of the epoxy ingredient filled up with silver when

it joined with this new paste ingredient, since the conductivity of a copper core was high is expectable. Moreover, by this metallic bond, conductivity stable also to heating and a heat cycle is acquired. Furthermore, it is also expectable that bonding strength becomes high with the combination of metallic bond and association by adhesives.

[0023] After the polymer component of a paste carries out desired thermal and functionalization suitable in order to acquire a hydrodynamic property, it can be used as the polymer which manufactured a refreshable raw material or a refreshable living thing from the ingredient made into a subject. A lignin (by-product of paper manufacture), a cellulose, tung oil, or a grain oil is a strong candidate for it. Since these ingredients can be obtained from a natural and refreshable raw material and can be easily processed rather than the conventional ingredient in the service life of an electronic assembly, it is desirable from an environmental standpoint to use these ingredients. Moreover, since the paste formula which it becomes unnecessary to use the solder containing lead (Pb), and is obtained is nonpoisonous and this is easy to dispose in order that it may use Cu-In powder, especially interest is held.

[0024] In case a conductive paste is prescribed, it is teaching using the copper powder coated with tin as a filler ingredient to the United States patent application No. 326626 specification which is application before this invention person. This copper powder is a globular form and is manufactured by the approach of the formation (atomization) of powder impalpable powder, or electrodeposition either. Coating of tin is performed on copper powder using the immersion plating liquid of tin. In order to obtain uniform coating of metal tin, it is desirable to wash carefully the oxide film on the front face of copper powder. Furthermore, during wet processes, such as etching, cleaning, a rinse, and filtration, and desiccation, it is not easy and, as for treating fines, time amount requires most.

[0025] That copper powder is a globular form has a certain kind of fault. In order to make the amount of a filler ingredient into the minimum and to raise conductivity, as for the gestalt of the high powder of an aspect ratio, the shape of a flake, tabular, etc. are desirable.

[0026] Since there is no immersion plating process in an indium metal, coating of the indium similar to the process which coats tin on above-mentioned copper powder to a copper powder top is impossible.

[0027] The process and structure of this invention give the solution approach of the problem of the powder of a globular form particle, and coating of an indium metal.

[0028] Drawing 5 is the schematic drawing showing what electrodeposited the thin indium metal 42 on the copper dendrite-crystal structure 44, after making copper dendrite-crystal structure adhere on the dummy substrate 40. As for the aspect ratio which are the die length of this dendrite crystal, and a ratio of width of face, it is desirable that it is about 1-10. The dendritic powder of the copper coated with the indium is easily recoverable by scratching from a dummy substrate using the cutting edge of a knife. The general conditions which make copper dendrite crystal generate according to electrodeposition are common knowledge in reference, for example, the bibliography quoted in the term of a Prior art. Drawing 6 and drawing 7 show the scanning electron microscope photograph of the dendrite-crystal structure of the copper generated by this invention. The used plating liquid mixes 1l. [79g CuSO4and5H2O and 200g (or 109ml) H2SO4, 0.116ml HCl, and] H2O. An anode plate is copper foil which does not contain

abbreviation 10cmx25cmx0.38mm (4 inch x10 inch x0.015 inch) oxygen. The ingredient of cathode is the rod of copper with a diameter of 3.2mm (1/8 inch) or nickel. In order to make expected dendrite-crystal structure generate on cathode, the plating process of a three-stage of growth of initial plating of the copper of (i) high density, the nucleation of (ii) dendrite crystal, and dendrite crystal (iii) is required. The typical three-stage plating conditions are as follows.

i) Initial plating 0.8 - 1.6 A/m2 (0.05 - 0.1A / inch 2) (0.1-0.2V) 0.02Ah (about 3 minutes)

ii) Dendrite-crystal nucleation 8 - 16 A/m2 (0.5 - 1.0A / inch 2) (0.8-1.2V) 0.1Ah (1 - 2 minutes)

iii) Dendrite-crystal growth 1.6 - 3.2 A/m2 (0.1 - 0.2A / inch 2) (0.3-0.7V) 0.1Ah (5 minutes)

Immediately after making copper dendrite crystal adhere, plating of an indium rinses cathode, puts it into a bath, and is performed by subsequently to an indium plating bath moving. Indium plating is performed at a room temperature using the sulfamide acid chloride of the indium made from AKONIAMU specia RUTI AROIZU (Arconium Specialty Alloys) of U.S. Rhode Island Providence. The conditions of typical indium plating are 0.8 - 1.6 A/m2 (0.1V) and 0.03Ah (about 3 minutes).

[0029] The process of the dendrite-crystal powder of the copper coated with the indium shown in this specification has some advantages as compared with the globular form copper powder which coated tin. It is the only approach to which an indium metal is made to adhere on copper fines the 1st in order to apply this process to a conductive paste. This approach does not need to manufacture the globular form copper powder at another process to the 2nd, and does not need the process which processes powder, such as etching, cleaning, filtration, a rinse, and desiccation, for it. Since indium plating can be performed to the 3rd immediately after growth of copper dendrite crystal, possibility that an oxide will generate on the front face of the exposed copper powder or dendrite crystal decreases. To the 4th, this approach generates the dendrite-crystal structure of copper with a larger aspect ratio than the globular form powder used by the conventional invention. for this reason, this ingredient -- the form of a conductive paste ingredient -- adding (10 - 90 % of the weight) -- electric and thermal conductivity increases. Finally, the main advantages of the dendrite-crystal ingredient of the copper plated with the indium are the conductive only high filler ingredient suitable for low-temperature assembly which can be used for the polymer substrate of FR-4 mold. An indium gets wet also to a ceramic type ingredient, and since the property is good, aluminum, titanium, chromium, molybdenum, tungstens, these oxides, etc. can use this ingredient also for the conductive pad which does not usually produce **** with solder.

[0030] Although this invention was attached and explained to the desirable example, many corrections, modification, and amelioration can be given to this contractor, without deviating from the principle and range of this invention.

[0031] As a conclusion, the following matters are indicated about the configuration of this invention.

[0032] (1) Structure characterized by for the above-mentioned dendrite crystal having the branching filament projected from the center section and the above-mentioned center section including the ingredient which is dendrite crystal, and carrying out coating of the above-mentioned dendrite crystal with the coating ingredient.

(2) Structure of the above (1) characterized by being chosen from the group which the above-mentioned ingredient becomes from Cu, Pd, Pt, nickel, Ag, and Au.
(3) Structure of the above (2) where some above-mentioned dendrite crystal [at least] is characterized by welding to other parts of the above-mentioned dendrite crystal through the above-mentioned coating.
(4) Structure of the above (2) where the melting point of the above-mentioned coating ingredient is characterized by being lower than the melting point of the above-mentioned dendrite crystal.
(5) Structure of the above (1) characterized by being chosen from the group which the above-mentioned coating ingredient becomes from In, Sn, Zn, Pb, Bi, and Sb.
(6) Structure of the above (1) where the above-mentioned dendrite crystal is characterized by being embedded into a polymer ingredient.
(7) Structure of the above (6) characterized by choosing the above-mentioned polymer ingredient as polyimide, a siloxane, a polyimide siloxane, epoxy, and a list from the group which consists of polymerization resin which uses living things, such as a lignin, a cellulose, tung oil, and a grain oil, as a raw material.
(8) Structure of the above (6) where the above-mentioned polymer ingredient is characterized by being thermoplastic adhesive.
(9) Structure of the above (1) where the above-mentioned coating is characterized by being conductivity.
(10) Structure of the above (1) where the above-mentioned structure is characterized by being an electric interconnect means.
(11) Structure of the above (1) where the aspect ratio which is a ratio of the die length of the above-mentioned dendrite crystal and width of face is characterized by being about 1 thru/or about 10.
(12) Interconnect structure characterized by having the branching filament which is interconnect structure including the 1st and 2nd front faces which interconnected with the ingredient which is dendrite crystal, and the above-mentioned dendrite crystal projected from the center section and the above-mentioned center section, and carrying out coating of the above-mentioned dendrite crystal with the coating ingredient.
(13) Structure of the above (12) where the above-mentioned coating is characterized by forming the metallic bond to the 1st and 2nd front faces of the above.
(14) Structure of the above (12) characterized by embedding the above-mentioned dendrite crystal into the polymer ingredient on which the 1st and 2nd front faces of the above are pasted up.
(15) Structure of the above (12) characterized by for the 1st front face of the above being the contact location of the 1st electronic instrument, and the 2nd front face of the above being the contact location of the 2nd electronic instrument.
(16) Structure characterized by the dendrite crystal with which it has the network of the dendrite crystal which has space, and which interconnected in between, the above-mentioned dendrite crystal has coating of a fusible ingredient, respectively, and it adjoins in the above-mentioned network having pasted up with the above-mentioned fusible ingredient.
(17) Structure of the above (16) where the above-mentioned space is characterized by including a polymer ingredient.
(18) Structure of the above (17) characterized by being chosen from the group which the

above-mentioned polymer ingredient becomes from polyimide, a siloxane, epoxy, and the polymerization resin that uses a living thing as a raw material.
(19) Structure of the above (16) where the above-mentioned fusible ingredient is characterized by being conductivity.
(20) -- the step which (1) cathode is immersed [step] in the plating liquid of the 1st metal, and makes the dendrite crystal of said 1st metal generate on said cathode surface, and (2) -- the manufacture approach of dendrite crystal which is immersed in the plating liquid of the 2nd metal in said cathode to which said dendrite crystal adhered, and contains the step which performs coating of the 2nd metal to said dendrite crystal.

[Translation done.]